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[54] METHOD FOR FORMING A PLATINUM RESISTANCE THERMOMETER

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Related U.S. Application Data

[63] Continuation of Ser. No. 104,575, Oct. 1, 1987, abandoned, which is a continuation of Ser. No. 636,141, Jul. 31, 1984, abandoned.

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|------|---|
| [52] | U.S. Cl |
| | 427/255; 427/259; 427/261; 427/282; 427/287 |
| [58] | Field of Search 427/101, 102, 103, 259, |
| | 427/255, 261, 287, 282; 204/192 C, 192 D; |
| | 428/207, 209; 338/25, 28, 368, 307, 314 |

[56] References Cited

U.S. PATENT DOCUMENTS

| 3,115,423 | 12/1963 | Dishworth | 427/102 |
|-----------|---------|----------------|-----------|
| 3,380,156 | 4/1968 | Lood et al | 29/620 |
| 3,617,373 | 11/1971 | Mott | 204/192 F |
| 3,645,783 | 2/1972 | Rupert et al. | 117/112 |
| 3,833,410 | 9/1974 | Ang et al. | 117/227 |
| 3,845,443 | 10/1974 | Fisher | 338/25 |
| 4,050.052 | 9/1977 | Reichelt et al | 338/308 |
| 4,072,593 | 2/1978 | Diehl et al. | 204/192 F |
| 4,085,398 | 4/1978 | Bertram | 338/25 |
| 4,103,275 | 7/1978 | Diehl et al. | 338/25 |
| 4,129,848 | 12/1978 | Frank et al | 338/308 |
| 4,181,755 | 1/1980 | Liu et al | |
| 4,353,935 | 10/1982 | Symersky | 427/89 |
| 4,375,056 | 2/1983 | Baxter et al | 338/25 |
| 4,510,178 | 4/1985 | Paulson et al | 427/94 |
| | | | |

FOREIGN PATENT DOCUMENTS

| 1014103 | 7/1977 | Canada | 204/192 F |
|---------|---------|------------------|-----------|
| 1597403 | 2/1978 | United Kingdom . | |
| 2096645 | 10/1984 | United Kingdom . | |

OTHER PUBLICATIONS

Waits, R. K., "Planar Magnetron Sputtering", Thin

Film Processes, Vossen and Kern, eds., Academic Press, N.Y., 1978, pp. 131-136.

Bennewitz, C. D. et al., "Structural and Electrical Properties of Films Sputtered from a Pt Cathode in Argon-Oxygen Mixtures", J. of Applied Physics, vol. 46, No. 2, Feb. 1975, pp. 558-567.

Thornton, J. A., Coating Deposition by Sputtering, Sep. 18-22, 1979.

Chapman, B., Glow Discharge Processes: Sputtering and Plasma Etching, John Wiley & Sons, N.Y., pp. 260-270. Vossen, John L. and Kern, Werner, eds., Thin Film Processes, Academic Press, N.Y., 1978, pp. 46-50 and 157-160.

Thornton, John A. and Penfold, Alan S., "Cylindrical Magnetron Sputtering", *Thin Film Processes*, John Vossen and Werner Kern, eds. Academic Press, N.Y., 1978, pp. 76-83.

Electric Phenomena, v. 97, 1982, p. 689, Abstract No. 97: 154621t.

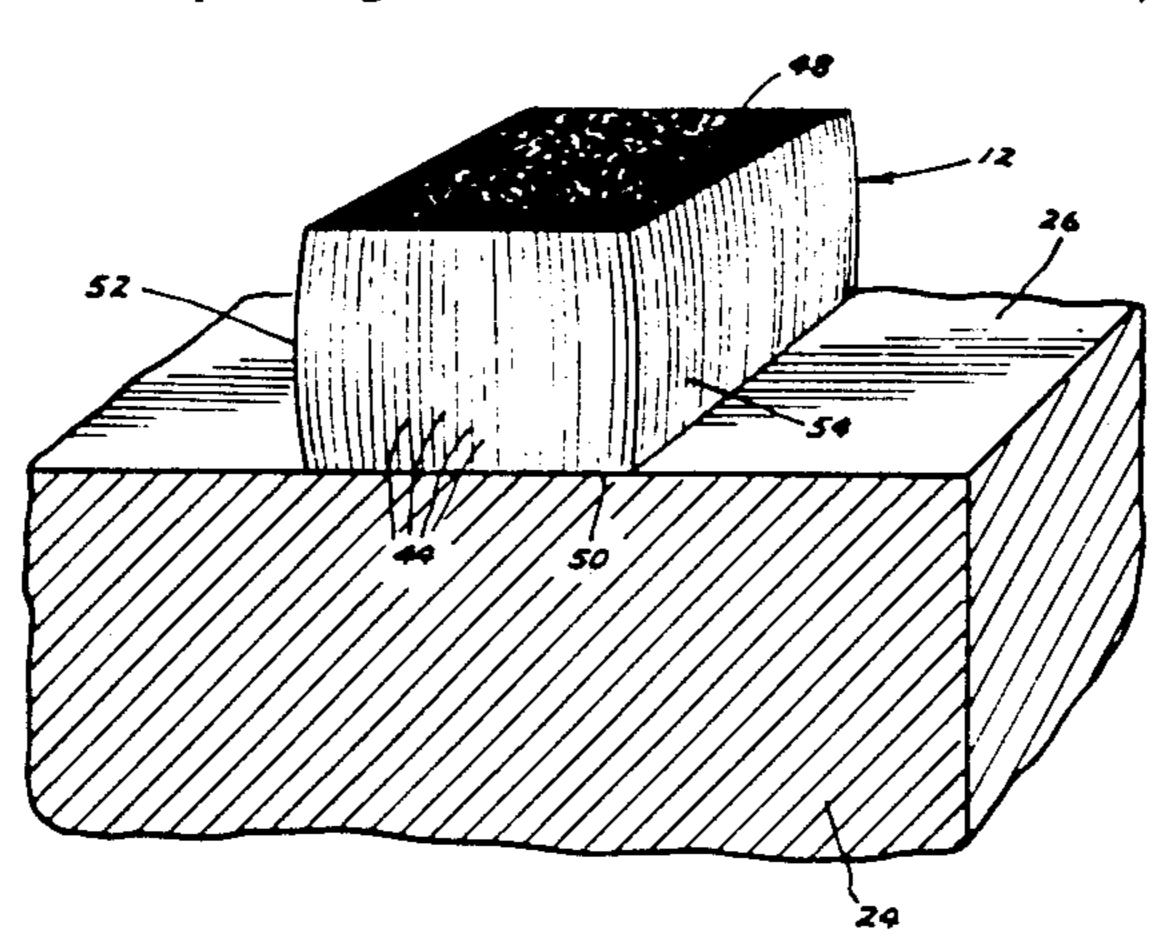
Chemical Abstracts, v. 91, 1979, p. 616, CA 220426n.

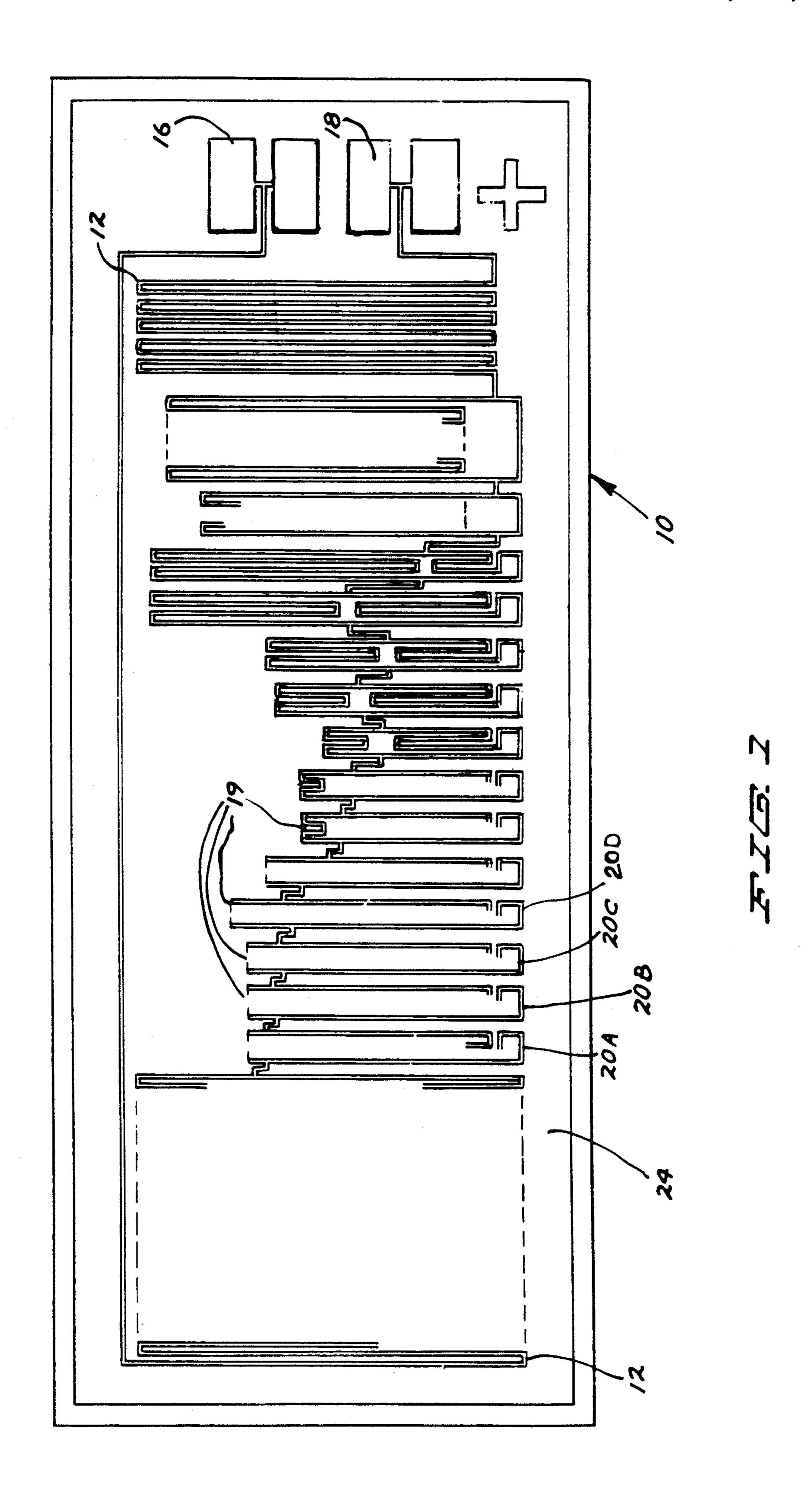
Primary Examiner—Janyce Bell Attorney, Agent, or Firm—Kinney & Lange

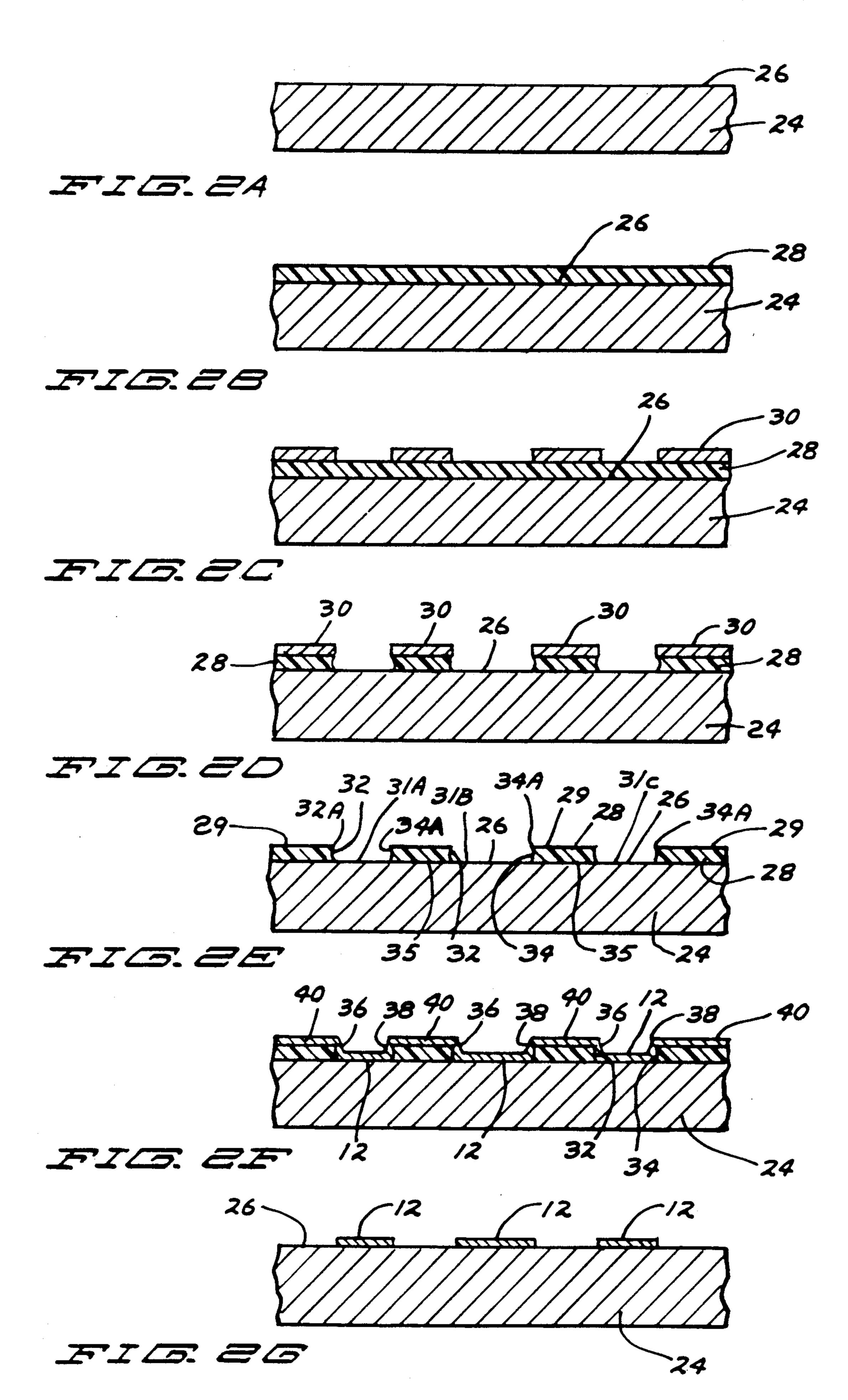
[57] ABSTRACT

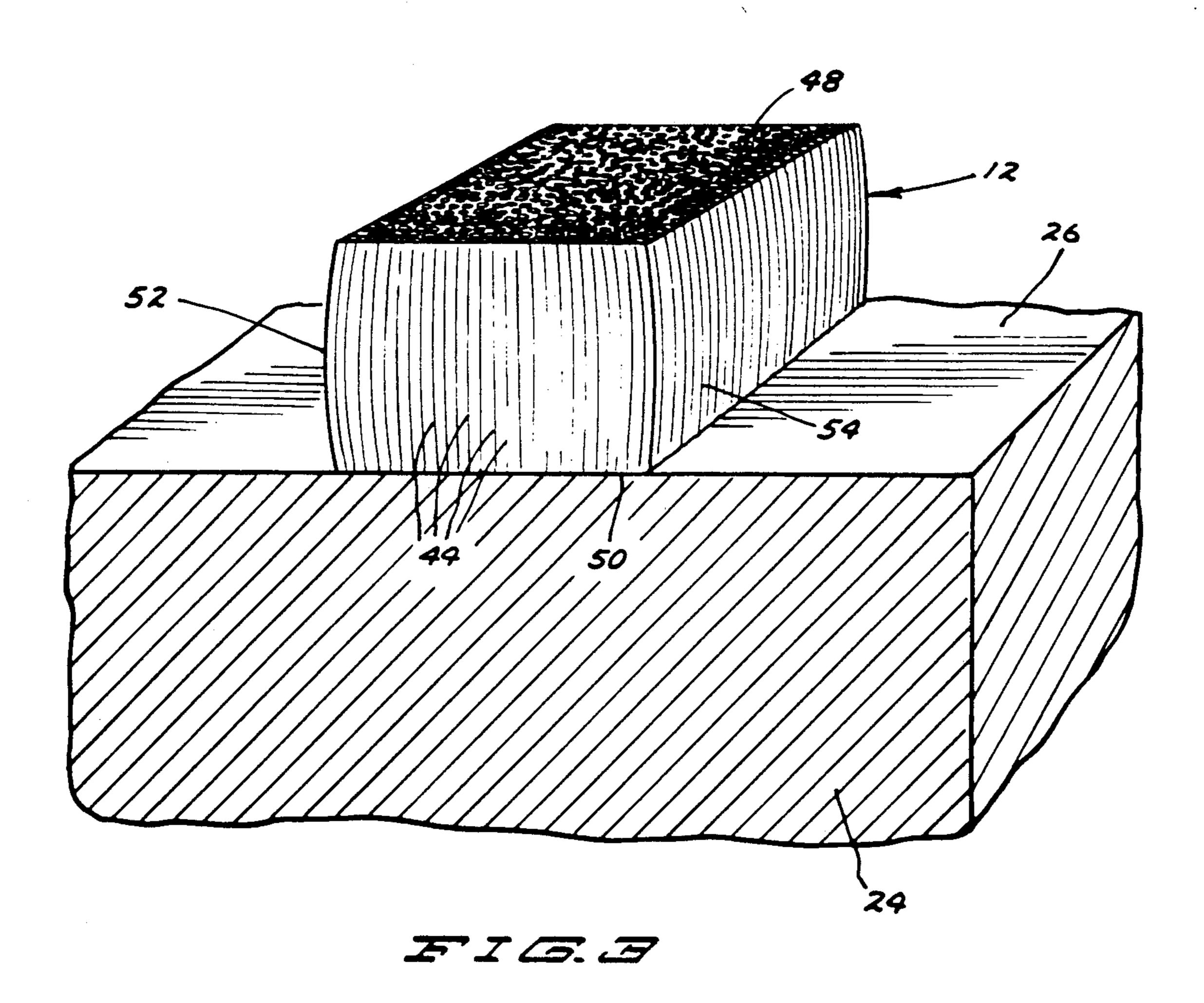
A platinum resistance thermometer is formed in a process which includes the defining of a path for the resistance thermometer in an inert material deposited in a layer on the substrate. The substrate surface is exposed in the path, and the inert material forms a negative pattern for the path. The resistive material for the thermometer is then deposited on both the substrate surface exposed in the path and on the surfaces of the inert material remaining on the substrate. After this, the inert material is etched away, and the resistive material deposited on top of the inert material is then loose and can be removed leaving a strip of resistive material in the desired path for forming the resistive thermometer. The strip has low contamination and impurities to more easily reach the desired temperature coefficient of resistance of the strip forming the thermometer.

17 Claims, 3 Drawing Sheets









METHOD FOR FORMING A PLATINUM RESISTANCE THERMOMETER

This is a continuation of application Ser. No. 5 07/104,575, filed on Oct. 1, 1987 which was a continuation of application Ser. No. 06/636,141, filed July 31, 1984 (both now abandoned).

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to methods of forming resistance thermometers that are easily made in a batch process and provide the desired characteristics.

2. Description of the Prior Art

Thin film platinum resistance thermometers are gaining acceptance, but there is a problem with obtaining the desired temperature coefficient of resistance (TCR) of the thermometer, and also, in order to obtain the desired nominal resistance, for example 100 ohms, a 20 platinum resistance element formed as a strip or ribbon of substantial continuous lengths made in a serpentine pattern of side by side strip sections. Making a thermometer which has a desired overall small size is difficult. The physical dimensions of the thermometer must 25 be precisely defined so that individual strip or ribbon sections can be placed close to each other, and the platinum strip or ribbon should have a uniform grain from edge to edge, and be free of contaminants to maximize the resistivity of the thermometer.

A process for producing a resistance thermometer element is disclosed in United Kingdom patent application Ser. No. 2,096,645, published Oct. 20, 1982. Magnetron sputtering under selected atmospheres is disclosed. The thermometer strip deposited is laser trimmed or 35 platinum is disclosed. scribed to define the size of the resistive strip. Controlling the atmosphere is emphasized in this publication in order to obtain a satisfactory thermometer.

Diehl et al. U.S. Pat. No. 4,072,593, issued on Feb. 7, 1978, discloses a process for reduction in size of a resis- 40 tance element for resistance thermometers. A platinum layer is sputtered onto an insulating solid, using a commercial RF sputtering apparatus and including forming "meanders" by means of a laser beam so that the resistance was standardized to 100 ohms. This patent dis- 45 closes methods of sputtering platinum onto a substrate, but does not suggest the use of a path defined in a separate liftoff material to obtain a desired resistance thermometer. The thermometer, after being formed with the desired pattern by a laser beam (or by photo etch- 50 ing) is tempered or heat treated.

Liu U.S. Pat. No. 4,181,755, issued on Jan. 1, 1980 discloses a way of generating a thin film pattern using a self lifting technique. The process involves depositing a continuous layer of circuit film onto the, surface of the 55 substrate, and then a photo resist pattern coincident with the ultimately desired circuit film pattern is defined on the surface of the circuit film. The portion of moved. While retaining the photo resist and the remain- 60 to be introduced into the platinum. ing circuit film, the entire surface of the substrate is coated with a barrier film. The photo resist is then stripped away from the surface of the circuit film causing the barrier film that covers the circuit, to liftoff, causing the circuit film to be exposed. The circuit film 65 pattern is then surrounded by a barrier film pattern. The device is used for making a Schottky barrier diode. In this instance, the barrier film is lifted off from a previ-

ously deposited conductor, and the patent does teach or suggest defining a platinum resistive path in an inert liftoff medium, depositing platinum material in the path and then etching away the liftoff medium to leave the thermometer in place.

Symersky U.S. Pat. No. 4,353,935, issued on Oct. 12, 1982 discloses a method of manufacturing a device having a conductor pattern that utilizes a liftoff technique to define at least one conductor. A multi layer 10 mask is required, and in the preferred embodiment the masking layer uses three sublayers of different materials, but it does provide recesses in the masking layer in the form of the conductive pattern that is to be provided. Etching is used, to expose part of the body sur-15 face through the masking layers, and then the conductive layer is deposited on both the masking layer and the exposed surface. The patent does not disclose the use of an inert material as a liftoff medium in which a thermometer pattern is formed and which liftoff material is removed after the platinum thermometer is deposited.

Bertram et al. U.S. Pat. No. 4,085,398, issued on Apr. 18, 1978 discloses a thin film resistance temperature detector using a copper mask, which is not useful in the present process, which requires an inert liftoff material. Other prior art of interest includes Diehl et al. U.S. Pat. No. 4,103,275, issued on Jan. 25, 1978 which discloses ionic etching for obtaining a resistance element for resistance thermometers, and Frank U.S. Pat. No. 4,129,848, issued on Dec. 12, 1978 which discloses a 30 platinum film resistor device which has a layer of quartz deposited upon an insulative substrate, which is sputter etched to produce etch pits in the surface for defining a path of the platinum thermometer. Chemical etching to expose the platinum for sputter etching away excessive

Reichelt U.S. Pat. No. 4,050,052, issued on Sept. 20, 1977, also discloses a temperature measuring resistor structure, comprising a resistance thermometer, having a strip of platinum applied to a carrier in a predetermined pattern, and discloses depositing the platinum strip while the temperature of the substrate is in the range of 500°-900° C. This patent also discloses heat treatment, but does not disclose any way of obtaining a sharply defined path as with the present process.

The prior art methods all tend to introduce impurities and cause the loss of definition at the edges of the platinum, thus affecting the TCR of the thermometer. For example, laser fabricating tends to melt the edges of the strip; photo etching gives impurities; ionic and sputter etching silicon or silicon dioxide causes deposition of this material into the platinum as impurities, and the platinum structure is affected or damaged at its edges so that there is a loss of definition. Use of masking in present techniques to etch away the platinum film in unwanted areas is a problem because the pattern cannot reasonably be defined with desired precision and uniformity for obtaining a small size and close spacing of the strip sections. The present masking layers tend to deterithe circuit film not covered by photo resist is then re- orate before the process is complete and impurities tend

SUMMARY OF THE INVENTION

A thin film resistance thermometer is formed on a suitable substrate which is substantially inert with respect to the resistance thermometer material. Preferably the resistance material is platinum, deposited on a substrate, such as sapphire, using known techniques which are selected to provide high purity platinum, which is **3**,007,**2**73

deposited so as to have a columnar grain pattern throughout the thermometer strip or path. The resistance thermometer material is formed in a strip having a meander or serpentine pattern by means of a liftoff process to obtain the desired resistance using as small a 5 surface section as possible.

To manufacture the thermometer, an electrically insulating substrate having a generally flat surface is provided. The substrate surface, is cleaned, and a raised layer of material that is readily etched away is formed as by deposition on the substrate. This material is called a liftoff medium and the medium must be substantially inert with respect to the platinum and substantially noncontaminating to the platinum. The desired pattern is formed as a recessed path in the liftoff medium. The surface of the substrate is exposed in the formed path, where it is desired to deposit the platinum thermometer strip.

Platinum is then deposited onto the substrate in the etched path, where the substrate is exposed, and also over the outer surface of the remaining liftoff medium, to a desired thickness. The depositing of platinum is preferably done by known sputtering techniques and under conditions necessary to obtain a continuous strip of substantially uniform and substantially pure columnar grain platinum suitably affixed to the substrate.

The layer of liftoff material is formed with sharply defined edge surfaces on the perimeter of the path defined for the platinum thermometer. The edge surfaces of the path are substantially normal to the substrate surface and this permits the columnar grain pattern of the platinum to form all the way to the side edges of the thermometer strip.

The deposited layer of platinum tends to be thin adjacent the upper edges of the perimeter of the path formed in the liftoff material. A thin band of platinum is thus formed above the thermometer strip extending to the outer surface of the liftoff medium. These thin bands of platinum are porous when compared to the material 40 deposited in the thermometer path. The thin bands thus permit liquid etch material to penetrate the platinum to act on the liftoff material, and the liftoff material is then etched away. The platinum deposited on the liftoff material and remaining outside the desired thermometer 45 path pattern is then unsupported and easily removed, leaving the platinum in the desired meander or serpentine pattern. The thermometer is a continuous strip or ribbon of substantially uniform crystal structure from edge to edge on the strip or ribbon forming the ther- 50 mometer. The edge surfaces of the path formed in the liftoff material are substantially normal to the substrate, such that the cross section of the thermometer strip is substantially rectangular and well defined without sharp or significant lateral protrusions or irregularities. 55

By using a liftoff medium and substrate which are substantially inert with respect to platinum, the purity of the platinum at the edges of the strip formed is maintained throughout its length.

The resulting structure of the platinum is well defined 60 columnar grains which provide a dense, uniform pattern, thus minimizing the size of the platinum resistance thermometer for obtaining the same resistance compared to a noncolumnar grain strip. Since there are no sharp irregularities or sharp lateral protrusions from the 65 sides of each path, (the liftoff medium defines smooth edge surfaces perpendicular to the substrate) the paths may be placed close together.

Impurities in the platinum and defects in the grain structure of the platinum have adverse affects upon the Temperature Coefficient of Resistance (TCR) of the platinum. The disclosed columnar grained structure of the platinum strip, which is uniform and substantially pure from edge to edge of the strip cross section, results in much greater control of the TCR of the platinum pattern. Thus yield of platinum resistance thermometers that achieve the required standard TCR of 3850 parts per million are greatly increased. Batch to batch variations are greatly reduced because of the control of structure and impurities.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an enlarged scale schematic diagram of a typical platinum resistance thermometer having a serpentine platinum strip pattern made according to the present invention defined on a substrate;

FIG. 2A is a greatly enlarged vertical sectional view of a portion of a typical substrate used for forming a resistance thermometer according to the present invention;

FIG. 2B is a sectional view corresponding to FIG. 2A, with a layer of liftoff medium shown deposited on an upper surface of the substrate with the thickness of the liftoff medium greatly exaggerated for clarity of illustration;

FIG. 2C is a sectional view corresponding to FIG. 2B showing a further step of processing including the deposition of a photo resist material after a desired path pattern has been exposed on the photo resist, and developed leaving the strip pattern in the photo resist over the outer surface of the liftoff medium;

FIG. 2D is a sectional view corresponding to FIG. 35 2C after the underlying liftoff medium has also been chemically etched in the areas not protected by photo resist, to define a serpentine path on the substrate for deposition of a platinum thermometer strip in such path:

FIG. 2E is a sectional view corresponding to FIG. 2D after the photo resist layer has been removed from the remaining liftoff medium, showing the substrate ready for deposition of the platinum thermometer material in the defined path;

FIG. 2F is a sectional view corresponding to FIG. 2E after deposition of a layer of platinum material by a sputtering process;

FIG. 2G is a sectional view of the finished platinum resistance thermometer showing the platinum meander paths in section, and corresponding to FIG. 2F, after the liftoff medium has been etched away and the platinum material deposited on the upper surface of the liftoff material has been removed; and

FIG. 3 is a detailed enlarged cross section representation of a platinum strip defined on the substrate in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

A batch fabricated platinum thin film resistance thermometer is indicated generally at 10 in FIG. 1. A platinum resistive strip or ribbon 12 is defined on a substrate 24 in a continuous, serpentine or meander path which is of length to provide a desired resistance utilizing a small, low mass substrate to improve temperature response characteristics. A requirement of thermometer 10 is that it have an industry standard Temperature Coefficient of Resistance (TCR) of approximately 3850 parts per million (ppm) such as listed in DIN (German

standard) 43760 or BS (British standard) 1904. Thermometer 10 may typically have a resistance of 100 ohms, although other resistance values also are standard, measured between a pair of electrical contacts 16 and 18 which are at the respective opposite ends of the strip 12. The thermometer desirably has a TCR of 3850 ppm ±3 ppm. The strip or ribbon 12 is formed in strip sections at least some of which sections can be trimmed out of the resistance strip to permit trimming the resistance value to a given resistance and tolerance after 10 fabrication.

Several resistive adjustments are provided for by severing the conductive strip 12 at selected locations indicated generally at 20A-20D. Selection and severing the conductive strip patterns at such locations is per-15 formed in a conventional manner to obtain the desired resistance value of 100 ohms or other specified value.

In the preferred embodiment showing severance of a conductive path 20A selectively eliminates one section of conductive path of the selected several pairs of parallel conductive path sections 19. Different conductive strip sections 19 are of different resistance values to provide for coarse and fine adjustment to obtain the desired overall resistance. Preferably, the conductive path sections 19 are physically separated from the 25 trimmable conductive path sections indicated at 20A-20D such that impurities introduced while severing them have little or no effect on the desired TCR or on the other desired resistive characteristics. Preferably, severing is performed by means of laser trimming. 30

Formation of the platinum strip 12 is done by defining a path in which platinum is deposited as described with reference to FIGS. 2A through 2G, which are of greatly enlarged scale. In FIG. 2A a section of substrate is shown in cross section. The substrate 24 is a non-conductive material which is substantially inert with respect to platinum over a wide temperature range and in reactive atmospheres or environments such as epitaxial grade (high purity) sapphire or aluminum oxide (alumina). Substrate 24 is relatively thin (vertical height), 40 but has sufficient strength to support the serpentine platinum strip. However, the substrate 24 for each thermometer has a low mass for fast temperature response and high strength for ruggedness.

A preferred material is high purity sapphire having a 45 polished surface 26. A ceramic alumina substrate or other materials having similar qualities can also be used. To remove potential impurities which interfere with adhesion and structure formation, the surface 26 of substrate 24 is cleaned in a sulphuric acid/hydrogen 50 peroxide solution.

After cleaning the surface 26 of the substrate 24, a layer of material 28 is deposited on the surface 26. This material is called a liftoff medium. The lift-off medium 28 preferably is a material such as silicon dioxide, which 55 is substantially inert with respect to platinum. In a preferred step, the liftoff material 28 is chemical vapor deposited to a preferred depth of about 25000 Angstroms onto the clean substrate surface 26 using a substantially pure tetra ethyl ortho silicate (TEOS) or sub- 60 stantially pure oxygen and silane sources. This chemical vapor deposition process provides a layer of substantially pure silicon dioxide, with very few atoms of free silicon which could later contaminate the platinum during deposition. A silicon nitride liftoff medium or 65 other inert liftoff medium will also function as the liftoff medium so long as the material selected does not react with platinum or with the atmosphere used when the

platinum is deposited, or tend to introduce impurities in the platinum or lose shape during platinum deposition.

As shown in FIG. 2C, a layer of photo resist 30, such as type KTI 747R, is next applied on top of the layer of liftoff medium 28. The photo resist is then exposed using a conventionally prepared negative mask, forming the desired serpentine or meander pattern for the path in which the platinum strip is deposited. The photo resist is then developed, and rinsed to expose the surface of liftoff medium 28 in the pattern or path which is the desired platinum path or pattern. The photo resist is exposed and developed preferably using stoddard solvent followed by an n-butyl acetate rinse, in a known manner, which does not introduce impurities which could have an adverse effect on the TCR of the subsequently deposited platinum.

A silicon oxide etch is then used to etch away the liftoff medium in the path pattern established in the photo resist. The etching is continued sufficiently long so that the substrate surface 26 is exposed in the desired platinum thermometer path, as shown in section in FIG. 2D.

A plasma resist strip or chemical strip is then used to remove photo resist layer 30 from the remaining liftoff medium 28 which is the negative pattern used to define the thermometer path as shown in FIG. 2E. It is important that all photo resist be removed at this stage in the process as it is a source of impurities that could contaminate the platinum that is deposited.

As stated, the liftoff medium 28 is preferably substantially pure silicon dioxide in the negative pattern with no free silicon, which is a potential impurity. Thus, care in using the known techniques to achieve the highest purity of the liftoff medium is desired.

The substrate surface 26 in the exposed path portions shown at 31A, 31B and 31C in FIG. 2E is now ready for deposition of platinum, the resistance thermometer material. Edge surfaces 32 and 34 of the continuous thermometer path are spaced to define the required width of the platinum strip. Edge surfaces 32 and 34 will be generally normal to the substrate surface and they are smooth, but are slightly concave due to the oxide etch acting on medium 28 along the sides of the path. However the lines or edges 32A and 34A (FIG. 2E) between the side surfaces of the path and the upper surface 29 of the remaining portions of the liftoff medium are sharp and well defined. The surfaces 32 and 34 are substantially planar and the undercutting amounts to only a slight bow in the cross section. Both the liftoff medium and the substrate must be inert with respect to platinum and are also chemically, and dimensionally, stable in platinum sputtering environments so that neither the liftoff medium 28 nor substrate 24 will diffuse into or react with the platinum.

As shown in FIG. 2F, a layer of platinum is then sputter deposited in a desired manner which may be as taught in United Kingdom Patent Application of Rosemount Engineering Company Limited No. 8124559, filed Aug. 11, 1981 and published Oct. 20, 1982, or as disclosed in Diehl U.S. Pat. No. 4,072,593, issued Feb. 7, 1978, onto the exposed surface 26 of substrate 24 in the path and also across line 32A and 34A onto the surface 29 of the remaining liftoff medium 28. Because care in the platinum deposition is important, reference is made to desired techniques outlined in a course manual for the American Vacuum Society, 1981, short course on Sputter Deposition and Ion Beam Processes sponsored by the American Vacuum Society, 335 East 45th

Street, New York, New York and specifically to Chapter VI of the course manual entitled "Coating Deposition by Sputtering" by John A. Thornton; and also to Chapter 4, of the book "Glow Discharge Sources For Sputtering" by W. D. Westwood, at pages 33-36. The platinum is preferably deposited at high temperatures in a reactive environment to obtain the desired grain orientation and purity.

In one preferred example, following cleaning of the surface of substrate 24 and the negatively patterned 10 liftoff medium 28 in FIG. 2E, substrate 24 was placed in a Materials Research Corporation, "Sputtersphere" Deposition Machine and preheated to 500° C. for a period of 10 minutes. The anode to cathode spacing was set at 2 inches and the machine was set for diode radio frequency sputtering. Initial pumpdown to 10-7 torr was obtained before proceeding. Sputter etching was performed at a power setting of 500 watts for 10 minutes to remove remaining surface contamination, using an atmosphere of substantially pure oxygen (99.97% 20 O₂) at an absolute pressure of 3.75 microns. Sputter deposition of 99.99 percent pure platinum was then performed at a target voltage of 1000 volts with a controlled substrate temperature of about 420° C.

The sputtering was performed for 360 minutes to produce a platinum layer 17000 Angstroms thick. The atmosphere was a reactive atmosphere of substantially pure oxygen (99.99 percent O₂) at 3.75 microns absolute pressure. The high substrate temperature for the long period of time of the preferred process, during which time the substrate is kept in a reactive environment, makes it important that substrate 24 and liftoff medium 28 are both substantially inert with respect to platinum and dimensionally stable to retain the required edge and line width definition.

Prior art liftoff medium materials such as photo resist tends to decompose and lose their structural strength, so the path side surfaces lose their shape in such an environment. The decomposition will introduce substantial impurities in the platinum path or pattern, and also the paths will lose definition because the side surfaces will round off at the top and will perhaps erode at irregular locations so the platinum is not well contained or defined. Photo resist materials and prior art liftoff medium materials also tend to diffuse into the platinum. Since the preferred liftoff medium, comprising silicon dioxide, does not react or significantly diffuse in the environment in which the platinum is sputtered, the surfaces 32 and 34 retain their shape and edges 32A and 34A remain 50 sharp line edges, so the platinum path retains the shape defined by the silicon dioxide negative pattern of material.

A table of preferred ranges and acceptable ranges for above described parameters and setting is set forth below:

TABLE I

| | PREFERRED | ACCEPTABLE |
|--------------------------|----------------------------|-------------------------|
| Substrate Preheat | | |
| Temperature | 500° C. | 200-500° C. |
| Anode to Cathode Spacing | 2" | 1-3" |
| Initial Pumpdown | $1 > 10^{-7} \text{ Torr}$ | 1×10^{-6} Torr |
| | | or l e ss |
| Sputter etch Power | 500 Watts | 100-1000 Watts |
| Time | 10 min. | 1-100 min. |
| Oxygen Pressure | 3.75 microns | 1-10 microns |
| Sputter Deposition | | • |
| Target Voltage | 1000 Volts | 750-1500 Volts |
| Substrate Temperature | 420° C. | 350-500° C. |

TABLE I-continued

| | PREFERRED | ACCEPTABLE |
|---------------------------|--------------|---------------|
| Time | 360 min | 300-600 min. |
| Target Platinum Thickness | 17000A | 14000A-30000A |
| Oxygen Pressure | 3.75 microns | 1-10 microns |

Variation of one or two parameters as much as $\pm 10\%$ can be tolerated so long as the other parameters are maintained, or adjusted so the overall quality of the thermometer does not degrade.

Preferably the platinum sputter deposition is conducted at a slow rate so the deposition time is long enough such that time of sputtering is not a critical factor and precise timing is not required. Stated another way, the time of deposition is capable of being controlled accurately enough for batch processing with repeatable results. Precise control of the thickness of the platinum is therefore easily obtained. Adding to the fact that a precise thickness is not crucial to obtaining desired TCR, it is seen that the platinum deposition step is easily controlled within desired limits to obtain required thickness of the platinum. Therefore, repeatability of the procedure is easily obtained even without overly precise controls on time. The deposited platinum has a columnar grain, as will be described, throughout the length, width and thickness of the strip, and reaches the desired TCR in batch processing.

An important feature of this method is its insensitivity to process variation. When etching away the liftoff medium to form the platinum path pattern, excessive undercutting of surfaces 32 and 34 can be a concern, but undercutting is easily monitored and controlled with known standard etching procedures. When stripping the photo resist used to define the platinum pattern in the liftoff medium, the stripping material disclosed does not adversely affect the liftoff medium or the substrate. so if stripping is continued for too long a time, no adverse effects are noticed. If the final liftoff etching conditions during the process unexpectedly vary, the variation will not likely cause scrapping of the substrate because the etching does not require critical solution strengths or timing. The etching steps must be continued long enough to remove materials which could result in defects.

It is important that materials proximate to the platinum do not react with platinum at high temperatures in a reactive environment or atmosphere so that harmful impurities are not introduced into the platinum.

The platinum layer is deposited to a thickness of approximately 17000 Angstroms, which is not as thick as the thickness (vertical height) of the layer of liftoff medium 28 (approximately 25000 Angstroms). Thus, as shown in FIG. 2F, after deposition of the platinum, the resistance thermometer strip or ribbon 12 does not have a thickness or height equal to the full height of the side surfaces 32 and 34 defining the path for the thermometer. Because the edges 32A and 34A do not round off as 60 the deposition progresses, thin bands of porous, interconnecting layer sections 36 and 38 of platinum form along the side surfaces 32 and 34 for the distance that the liftoff medium layer 28 extends outwardly in thickness beyond 17000 Angstroms, which is the deposited 65 platinum strip height or thickness in the paths. The bands 36 and 38 form thin porous bands of platinum approximately 8000 Angstroms wide adjacent the edges 32A and 34A along the entire path.

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Platinum thickness of the platinum thermometer strip deposited in each path may range from 14,000 Angstroms to 30,000 Angstroms if desired provided the thickness of the liftoff medium 28 is correspondingly changed so that it is always thicker than the desired 5 thickness of the platinum strip. The liftoff medium 28 preferably has a thickness of at least 1.3 to 1.5 times the thickness (height above surface 26) of the platinum that is deposited.

The thin band sections of platinum 36 and 38 are 10 generally sufficiently porous so that a liquid etchant will penetrate the thin strip layer sections. An etchant such as hydrofluoric acid, which has little effect on either platinum or the substrate 24, is then used to etch away the remaining parts of the liftoff medium. Since the 15 etchant has little effect on the platinum or substrate the timing and temperature of the etch of the final liftoff medium is noncritical and has little effect on the yield of acceptable thermometers from a substrate, that is, normal variations in time and temperature of the final etch- 20 ant will not result in an increased scrap rate. After etching all of the liftoff medium away, the portions of the platinum layer indicated at 40 which were deposited on top of the liftoff medium may be mechanically separated from the upper edges of the platinum thermome- 25 ter strip or ribbon 12 in the region of the thin bands 36 and 38. This can be accomplished by lifting the sections 40 or by rubbing the platinum with a suitable pad to break off sections 40. The thermometer strip or ribbon 12 is tightly bonded to the substrate surface so it will not 30 come loose. The thin platinum bands 36 and 38 are also rubbed to remove any thin or irregular edges on the strip 12, which would tend to break off in use and change the overall resistance of thermometer 10. FIG. 2G illustrates the device at this point in the process.

An optional step may be performed to aid etching away the liftoff medium if desired. Before liftoff medium 28 is etched away, a mild platinum etch may be used to etch the thin bands 36 and 38 for approximately five to fifteen minutes with, for example, a solution 40 consisting of 10H₂O: 9HCl: 1HNO₃. The thickness of the platinum strip 12 on substrate surface 26 is not appreciably affected by such mild etch, but the thin bands 36 and 38 are substantially removed during such an etch step because the bands are very thin and porous as com- 45 pared to the thermometer strip or ribbon 12 secured to substrate surface 26. When the thin bands 36 and 38 are substantially removed by the optional platinum etch, liftoff medium 28 in the negative pattern is then etched away as described above and the platinum layer sections 50 40 are easily removed because they will be loose, and can be blown off by a gas flow across substrate surface **26**.

Thermometer 10 is then cleaned as desired, and is then heat treated for approximately six hours at a temperature of 1000° C. in an oxygen atmosphere. The heat treatment does not remove the columnar crystal structure, but only compacts the film. Thus, during heat treatment, the thickness of platinum strip or ribbon 12 above the substrate surface decreases to approximately one half of the deposited thickness (7000 Angstroms to 15000 Angstroms), and the conductivity of the platinum strip or ribbon 12 increases. The heat treatment temperature may vary from 800° to 1000° C. and the thermometer is heat treated for between five and seven hours.

It has been found that a platinum strip thickness (above the substrate) after heat treatment of at least 7000 Angstroms provides the desired TCR. During

initial heat treatment, the TCR and the platinum resistivity change quickly, but then change relatively slowly toward the end of the heat treatment so that the TCR and platinum resistivity do not vary significantly from batch to batch, with reasonable time controls.

In FIG. 3, wherein the numbering is consistent with the foregoing figures, the structure of the platinum strip or ribbon 12 is shown in enlarged cross section, and when the platinum is deposited as described comprises closely packed columnar grains 44 of platinum. The grains 44 are preferably substantially continuous in length in the thickness or height direction of the strip. and have longitudinal axes normal to substrate surface 26. A substantial portion of the grains are continuous if the sputtering is done carefully as described. The platinum strip structure comprises a top surface 48, a bottom surface 50, which is bonded or secured to or interfaced with substrate surface 26, a first side surface 52 and a second side surface 54. First side surface 52 and second side surface 54 are smooth, but curve very slightly outwardly (they are convex) corresponding to the slight inward curve or concavity of surfaces 32 and 34 of the liftoff medium.

The columnar grains 44 are uniformly dispersed substantially over the entire section of strip or ribbon 12 out to first side surface 52, and to second side surface 54, due to the structural stability of the liftoff medium during deposition of the platinum. Thus, substantially the entire strip has the columnar grain. The paths for the platinum strip or ribbon 12 remain sharply defined in the liftoff medium during deposition of the platinum.

Since the liftoff medium 28 is inert with respect to platinum and dimensionally stable in the sputtering environment, few impurities or structural defects occur 35 at first and second side surfaces 52 and 54. Thus, first and second side surfaces 52 and 54 are well defined, smooth, and are substantially normal to substrate surface 26. This provides yet a further benefit in that the platinum paths may be formed or placed closer together, so that the platinum strips are closer together. If the sides of the paths in the liftoff medium exhibit significant lateral protrusions, are not structurally intact, or tend to spread out over the surface of the substrate as the platinum is deposited, there is an increased probability of electrically shorting between the sections of the strip or ribbon formed in the paths. With the structure of platinum shown in FIG. 3, the desired TCR is obtained and a smaller thermometer size is achieved because of the well defined sides of the strip or ribbon sections. A platinum strip width of 20 micrometers with a distance of 20 micrometers between the strip sections is easily batch fabricated using the above described liftoff technique.

The liftoff technique permits smaller thermometer size regardless whether the platinum is deposited in a columnar structure or not. Because of the non-reactive structurally stable materials used for the liftoff medium that defines the paths, the side surfaces of each path are well defined and substantially free of impurities. If the side surfaces have impurities or are not well defined, the TCR of the deposited platinum will be lowered. Of course, the bulk or volume of the platinum is an important consideration for achieving the TCR.

With low levels of impurities in the platinum, the platinum strip thickness must be increased to increase the TCR. With increased thickness of the strip 12, the sheet resistivity decreases and the strips must be made narrower, or longer, to obtain the desired operating

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resistance for the thermometer. Prior means of pattern definition introduce substantial impurities in the platinum along the edges. Hence making the pattern narrower with prior processes introduced more impurities and further lowered the TCR. Thus, a longer, more 5 extensive strip or ribbon pattern was needed to obtain desired resistances and TCR's in prior art devices. With high levels of impurities in the platinum the thermometer will never reach the desired TCR.

The added benefit of the columnar platinum grain 10 structure is that even more control of the TCR is obtained with excellent repeatability. The precise thickness of the platinum layer having the columnar grain structure is not significant with respect to the TCR of the strip or ribbon in the selected range of platinum 15 thicknesses. Thus precise timing of the platinum deposition is not required, and successful processing of each batch is greatly enhanced under commercial conditions.

Although the present invention has been described with reference to preferred embodiments, workers 20 rial is epitaxial grade sapphire. skilled in the art will recognize that changes may be made in form and detail without departing from the spirit and scope of the invention.

What is claimed is:

1. A process for making a thin film platinum resis- 25 tance thermometer comprising the steps of:

providing a substrate substantially noncontaminating to platinum and having an upper surface; depositing a layer of liftoff medium which is substantially noncontaminating to platinum onto the substrate 30 upper surface to leave an exposed surface of liftoff medium, the liftoff medium being chemical vapor deposited such that free atoms of the liftoff medium are at a low level, and removing portions of the liftoff medium to expose the substrate surface in a 35 path defined through the liftoff medium comprising a negative pattern from a predetermined pattern desired for the resistance thermometer, the removing of the portions of the liftoff medium comprising etching the liftoff medium under con- 40 trol so as to form sharp edges at the junction of the path and the exposed surface;

depositing platinum on the exposed portions of the substrate and on the exposed surface of the liftoff medium; and

- removing the liftoff medium and platinum deposited on the liftoff medium while leaving the platinum secured to the exposed substrate surface in the path, the platinum secured to the exposed substrate remaining substantially uncontaminated by the 50 liftoff medium including free atoms of the liftoff medium.
- 2. The process of claim 1 including the steps of first depositing the liftoff medium onto the entire substrate surface and the steps of removing comprises etching 55 away the liftoff medium to define the path with etched side surfaces defined in the liftoff medium extending upwardly from the substrate surface to define the sharp edges.
- 3. The process of claim 2 including the step of etching 60 the liftoff medium off the substrate after depositing the resistive material and removing resistive material not in the defined paths.
- 4. The process of claim 3 in which the resistive material deposited in the path is of a thickness less than the 65 thickness of the liftoff medium so the side surfaces defining the path extend upwardly more than the thickness of the path to thereby cause porous strips of the

deposited resistive material to be formed adjacent the outermost portion of such side surfaces for permitting liquid etch to be used on the liftoff medium.

- 5. The process of claim 4 wherein the platinum is sputter deposited in a reactive atmosphere under elevated temperatures at a rate so as to provide the columnar grain platinum oriented generally normal to the substrate surface in a process wherein time control is not critical.
- 6. The process of claim 5 wherein the liftoff medium is selected to resist reaction with and diffusion into the atmosphere used for depositing the platinum to retain the sharp edges along the path and to maintain the side surfaces substantially perpendicular to the substrate throughout the exposure to the resistive material deposition environment at temperatures to 500° C.
- 7. The process of claim 6 wherein the liftoff medium is TEOS derived SiO₂.
- 8. The process of claim 6 wherein the substrate mate-
- 9. The process of claim 6 wherein the liftoff medium is a chemical vapor deposited oxide of silicon.
- 10. A process for making a thin film platinum resistance thermometer comprising the steps of:
 - providing a substrate substantially noncontaminating with respect to platinum and having an upper surface;
 - depositing a layer of a liftoff medium which is substantially noncontaminating with respect to platinum and dimensionally stable under temperatures encountered in the process onto the substrate surface in an area large enough to encompass the thermometer to be formed, the thickness of the liftoff medium relative to the substrate surface being greater than the desired thickness of the thin film platinum used to form the thermometer on the substrate;
 - etching away the liftoff medium under a controlled etch to expose the substrate surface in a continuous path defined through the liftoff medium, the etching being time controlled to form side edges of the path which are smooth and substantially perpendicular to the substrate surface, and stopping the etching process while the side edges are substantially free of undercuts;
 - depositing the platinum over the exposed portions of the substrate and over the liftoff medium at a rate which produces a columnar grain structure in the platinum, so that the platinum is deposited on the exposed portions of the substrate in the continuous path to provide a columnar grain platinum ribbon in the path, and which depositing extends the platinum along the side edges of the path above the platinum ribbon to join the platinum deposited on the surfaces of the liftoff medium; and
 - removing the liftoff medium and the platinum material deposited on the liftoff medium while leaving the platinum substantially uncontaminated by the liftoff medium and secured to the exposed substrate surface in the path, whereby the columnar grain of the platinum provides a high temperature coefficient of resistance.
- 11. The process of claim 10 wherein the depositing of the platinum is at a rate which causes a thin layer of the platinum to be formed at the junction of the sides of the path and the liftoff medium, to form thin band sections that are porous above the platinum ribbon, and wherein the step of etching includes use of a liquid etchant that

penetrates through the thin band sections to etch the liftoff medium and leave the deposited platinum in place, and including the steps of removing the platinum layer initially deposited on the liftoff medium, by separating it from the upper edges of the deposited platinum 5 ribbon in the region where the thin band section of platinum is formed along upper portions of the sides of the path formed in the liftoff medium.

- 12. The process of claim 11 including the further step of removing thin and irregular edges on the deposited 10 ribbon to the upper corners thereof.
- 13. The process of claim 10 including the further step of etching away portions of the platinum in the regions where the platinum is deposited in the path above the platinum ribbon prior to etching the liftoff medium.
- 14. The process of claim 10 including the step of depositing a layer of liftoff medium to have a thickness of in the range of at least 1.3 times the thickness of the desired platinum ribbon to be deposited.
- 15. The process of claim 10 including the step of 20 to 10 microns. depositing the liftoff material as a layer of silicon diox-

ide to reduce diffusion and reaction with the environment in which the platinum layer is deposited, so that the sides defining the path retain their shape and form sharp line edges at the upper junction of the sides of the path and an outer surface of the liftoff medium.

- 16. The process of claim 15 wherein the depositing step is a sputtering step, and wherein the substrate is preheated prior to sputtering.
- 17. The process of claim 16 wherein the substrate is preheated to in the range of 200° to 500° C. in a reactive atmosphere, and a sputtering etch is used to clean the substrate surfaces in the path, and the platinum is then sputter deposited over a substantial period of time using a target voltage of between 700 and 1500 volts, a substrate temperature of in the range of 350° to 500° C., and that during a time of 300 to 500 minutes a platinum film of in the range of 14,000 to 30,000 Angstrom units is applied, using an oxygen atmosphere at a pressure of 1 to 10 microps

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UNITED STATES PATENT AND TRADEMARK OFFICE CERTIFICATE OF CORRECTION

PATENT NO. : 5,089,293

DATED: February 18, 1992

INVENTOR(S): ROBERT C. BOHARA ET AL.

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Col. 1, line 55, delete "the,", insert "the"

Col. 2, line 28, after "Frank", insert "et al."

Signed and Sealed this Twenty-sixth Day of May, 1992

Attest:

DOUGLAS B. COMER

Attesting Officer

Acting Commissioner of Patents and Trademarks